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ECONOMIC AND ECOLOGICAL EFFECTS OF THE COPRODUCTION OF NITRIC ACID AND ELECTRIC AND THERMAL POWER USING STEAM-GAS TECHNOLOGIES

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Nitric acid (HNO_3) is a high-tonnage product of the chemical industry, which has come into widespread use in various processes of chemical technology, especially in the mineral-fertilizer industry. The annual world production of HNO_3 has reached 60 million tons [1, 2], and is tending to increase. The production of nitric acid in countries of the former USSR is approximately 17 million tons/year.

With such a massive product yield, problems of the optimal design and operation of production and power plants are basic from the standpoint of operating costs and ecology; this is associated with the following specifics of this production process:

• a large amount of the heat liberated in the process, including high-temperature heat (the heat of exothermal reactions with allowance for condensation and dilution of the acid amounts to 7,149 MJ/ton of HNO_3); and

• a large amount of compressed air required for the production process (oxygen and ammonia are raw materials for the production of HNO_3) and post-production tail gas discharged to the environment (4.75 tons of air/ton of HNO_3, and 3.73 tons of tail gas/ton of HNO_3).

Let us examine a method of reducing operating costs, which utilizes the heat of the exothermal chemical reactions and which is more effective than that of classical systems employed for the production of HNO_3. This is possible when the production process is combined with the steam-gas process used for the production of electric power and effective heat.

In the classic scheme employed to produce nitric acid with a single pressure (Fig. 1), the machinery consists of a compressor, which supplies air for the catalytic oxidation of ammonia to nitric oxide (NO) and its conversion to nitrogen dioxide (NO_2) in an absorption column, where nitric acid HNO_3 is formed with the participation of water, and also a tail-gas expander (approximately 98% of nitrogen, 2% of oxygen, and from 50 to 100 ppm of NO_x) for driving the compressor. A condensing steam turbine, which is supplied with steam from a waste-heat boiler incorporated in a series of heat exchangers for the process-gas cooling system, serves as an additional drive of the air compressor. The temperature distribution of the tail gas in this cycle (Fig. 2) depends on the design assumptions with respect to the distribution of heat output for the gas and steam cycles in the power system of the plant producing the HNO_3, i.e., above all, for the steam turbine and expander, as well as for the amount of heating and process steam output externally (so-called export). The method used to extract the NO_x from the exhaust gas to support the requirements for environmental protection may exert a significant influence on the output distribution of these cycles. In modern HNO_3 production, two principal methods are basically used for the catalytic reduction of the NO_x: selective ammonia (SCR), and also natural gas [3]. The chemical reactions in both methods are exothermic; moreover, the temperature rise of the exhaust gas (SCR method) is only 10°K (for an optimal temperature range of from 230 to 330°C). Reduction of the NO_x by natural gas using catalysts with favorable metals provides for an increase of approximately from 200 to 300°K when

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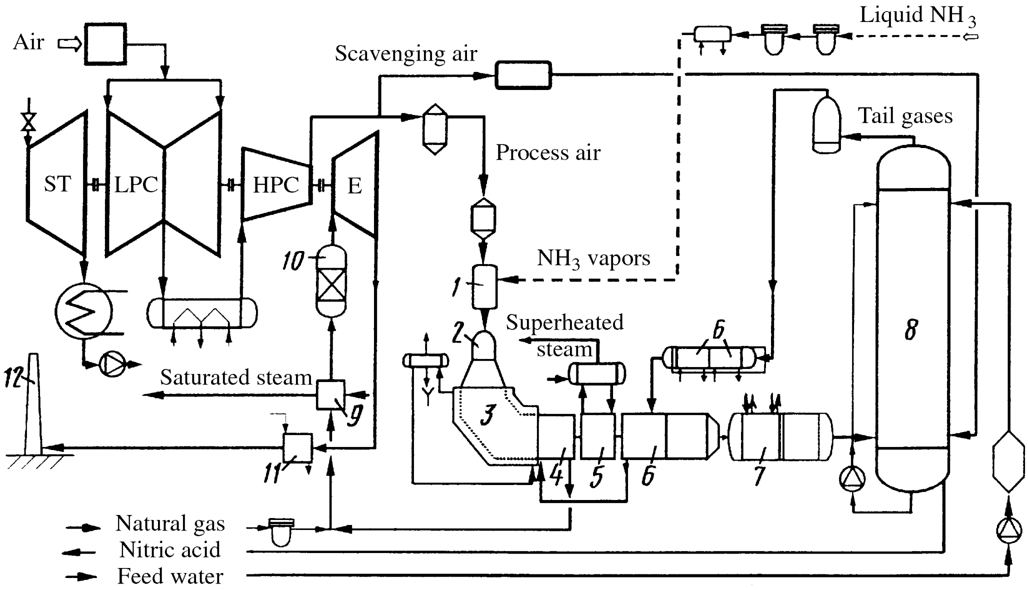

Fig. 1. Schematic diagram of nitric-acid production: *1*) air and ammonia-vapor mixer; *2*) catalytic reactor; *3*) reactor bend; *4*) heat exchanger of expander; *5*) high-pressure waste-heat boiler; *6*, *7*) heat exchangers of tail and exhaust gases, respectively; *8*) absorption column; *9*) superheater; *10*) combustion chamber (catalytic removal-reduction of NO_x; *11*) economizer; *12*) pipe; ST) steam turbine; LPC and HPC) low- and high-pressure compressors, respectively; E) expander.

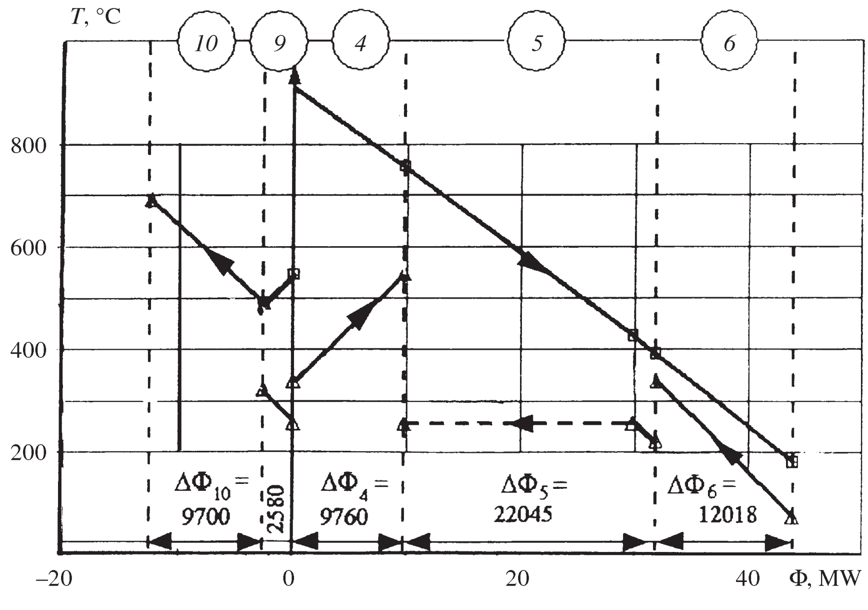

Fig. 2. Distribution of temperatures *T* and flows Φ in heat-exchange system for nitric-acid plant with output of 1000 tons/day (figures *4*, *5*, *6*, *9*, and *10* correspond to the designations in Fig. 1).

the temperature at the inlet to the catalyst is of the order of 480–530°C (spontaneous combustion of methane occurs at 560°C). In the reduction process, concentration of NO_x to 50 and 20 ppm is possible – in the exhaust gas prior to the expander.

The air compressor, exhaust-gas expander, and reactor for the catalytic reduction of nitric oxides (see Fig. 1) are, in principal, a gas turbine (gas-turbine engine), and together with the system utilizing the exhaust heat, is a combined steam-gas heating plant, which supplies heat for heating or production purposes. Fitting-out of the system additionally with an electric gen-

TABLE 1

Type of drive system	Total thermal efficiency $(\eta_C)_{COMB}$
GTT-3 gas turbine	0.4335
Electric motor + expander	0.3264
Condensing turbine + expander	0.1514
Back-pressure turbine + expander	0.3065

erator and reducing the amount of heating steam vented externally transforms the heating plant into an electrothermal plant, which utilizes the heat of the catalytic oxidation of the ammonia and produces electric power and effective heat in combination with the HNO_3-production system, i.e., **provides for the coproduction of nitric acid, electric power, and effective heat**.

This technical solution has, however, a number of drawbacks:

• the production system consists of individual machines and vessels (with separate bearings), which are coupled in a single line frequently with different rotational speeds (gearing) and with differing thermal expansion and axial forces having variable values and directions; and

• low parameters of the working substances in the gas and stream cycle and inadequate efficiencies of the turbo-machinery; this is a principal cause of incomplete utilization of the heat of the exothermic reactions in the synthesis of HNO_3.

Operational problems with exhaust-gas expanders are known to us, even within the temperature limits from 600 to 650°C; there are also data from the United States, especially with respect to thermal expansion and its effect on bearing longevity, a highly uniform consumption of cooling air, etc.

Basic improvement of the steam-gas system for the nitric-acid plant, and its transformation to a steam-gas plant may support the use of a gas-turbine-driven generating set with a liquid fuel gas (natural gas is best, since it is widely used as a raw material in the chemical industry) in lieu of the compressor-expander system.

Let us analyze a proposed variant with a gas-turbine-driven generating set, which is connected to the HNO_3-production system. Here determination of the total thermic efficiency of the generation of electric power and heat assumes major significance:

$$(\eta_C)_{COMB} = \frac{P_{eGT} + P_{eST} + \dot{Q}_U}{\dot{Q}_{RC} + \dot{Q}_F},$$

where P_{eGT} and P_{eST} are the effective horsepowers of the gas and steam turbines, respectively, $\dot{Q}_U$ is the effective-heat flux, and $\dot{Q}_{RC}$ and $\dot{Q}_F$ are the heat fluxes, respectively, of the chemical reactions and fuel supplied.

For combined steam-gas electric power plants, which are not coupled to the heat liberated by chemical reactions ($\dot{Q}_{RC} = 0$), and which produce only electric power, this relationship takes on the form of the fuel efficiency of the combined cycle:

$$(\eta_{the})_{COMB} = \frac{P_{eGT} + P_{eST}}{\dot{Q}_F} = (\eta_{the})\left(1 + \frac{P_{eST}}{P_{eGT}}\right),$$

where $\eta_{the} = P_{eGT}/\dot{Q}_F$ is the effective fuel efficiency of the gas turbine.

The heat flux from the chemical reactions is determined considering that the total amount of heat liberated by the chemical reactions in HNO_3-production systems $q_U = 7.149$ GJ/ton of HNO_3, including the heat of condensation and dilution of the nitric acid [4].

Let us examine the power-production system of machines with a GTT-3 turbine in the production of nitric acid. A detailed efficiency analysis of various power systems and the significant advantage of the system with a GTT-3 gas turbine over other systems used to drive process-air compressors are presented in [5] (Table 1).

The GTT-3 gas expander with a relative process-air extraction $\delta_A = 0.91$ drives (via gearing) a two-stage centrifugal compressor in parallel (the high-pressure section of the axial-flow turbine-driven generating set), as well as an asynchronous motor – generator with a rated power of 165 kW. The turbine is equipped with two combustion chambers: a start-up chamber (on natural gas), and a main chamber, which serves simultaneously as a catalytic reactor for the reduction of NO_x by natural gas,

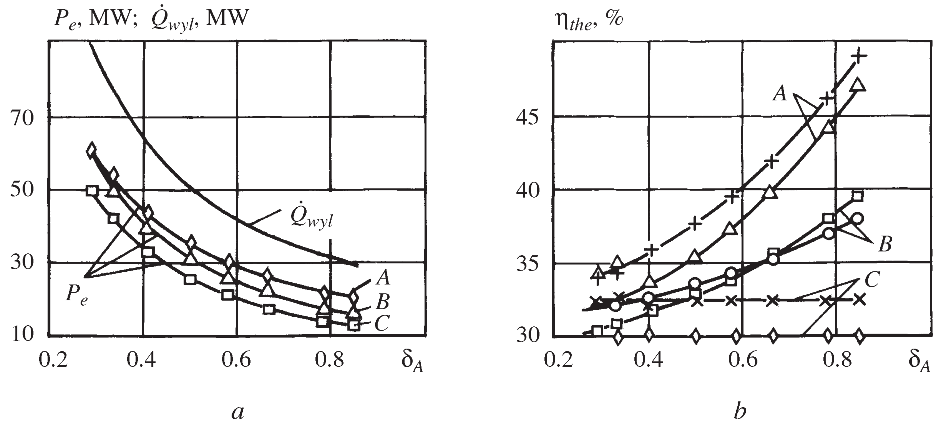

Fig. 3. Dependence of effective capacity P_e, thermal flux $\dot{Q}_{wyl}$ of exhaust gases (*a*), and effective efficiency η_{the} of compressor (*b*) on relative steam extraction δ_A and compression ratio π: *A*) with intermediate cooling; *B*) without cooling; *C*) simple cycle; Δ, ❏, ◊) $\pi = 11$; +, ❍, ×) $\pi = 15$.

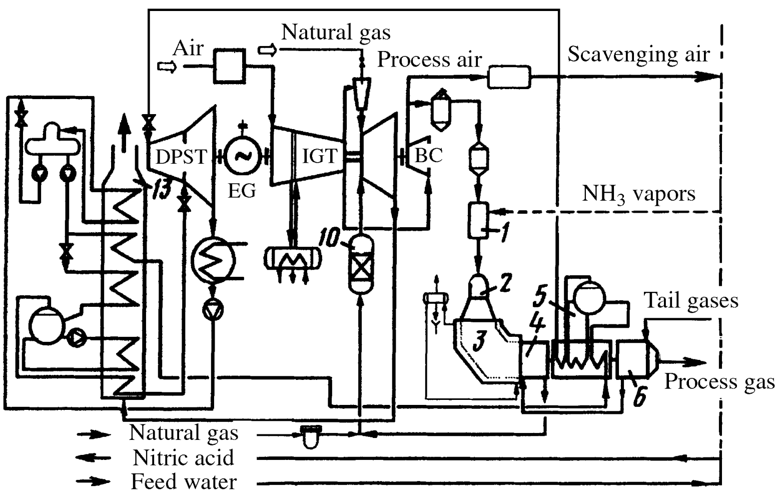

Fig. 4. New alternate scheme for nitric-acid production: *1–5, 10*) same as in Fig. 1 (vessels *6–9*, *11*, and *12* are not included in this scheme); *13*) atmospheric waste-heat boiler; DPST) steam condensing turbine with steam extraction; IGT) industrial gas turbine; EG) generator; BC) additional compressor.

and heats the exhaust gas (due to the heat of the reaction) to 700°C prior to the turbine (the maximum temperature does not exceed 730°C). Both waste-heat boilers – charged (in a system where process-gas heat is utilized) and atmospheric (beyond the gas turbine) – are supplied with water vapor only for heating requirements.

Operational difficulties of such a system for operation of a gas-turbine generating set, which are caused by low electric power, are underscored in [5]. Minor contamination of the axial-flow compressor and interstage heat exchanger is sufficient to render the heat balance of the turbine capacity negative. When it is necessary for the customer to maintain capacity, water vapor can be injected into the turbine (1 ton/h of additional vapor increases the turbine capacity by 75–80 kW while lowering the temperature prior to the turbine simultaneously by 7–8°K).

Let us propose an alternate scheme for the new production solution of the power system in the production of HNO_3 – a turbine-driven generating set with process-air extraction and the addition of tail gas to the combustion chamber.

When integrated with an HNO_3-production system, such a gas-turbine system should perform the following tasks:

• supply some of the air from the compressor for the turbine-driven generating set into the system; and

• expand the remaining air, which is heated to the appropriate temperature in the combustion chamber and mixed with the tail gas heated in the heat exchangers of the system’s heat-recuperation unit, in the turbine of the turbine-driven generating set.

TABLE 2

Relative extraction δ_A	Fuel efficiency		Effective power, MW			Total efficiency of combined cycle $(\eta_C)_{COMB}$	
	gas turbine η_{the}	combined cycle $(\eta_{the})_{COMB}$	gas turbine P_{eGT}	steam turbine P_{eST}	total	$(P_{eST})_{\max}$, $Q_U = 0$	$P_{eST} = 0$, $(Q_U)_{\max}$
0.7	0.410	0.759	21.0	17.9	38.9	0.352	0.70
0.4	0.335	0.552	41.0	26.6	67.6	0.330	0.60

TABLE 3

Indicator	δ_A	Entire world	United States	Countries of former USSR	Countries of European Community	Germany	Poland
Total capacity, MW	0.7	7002	992	1983.9	1925.6	245	245
	0.4	12168	1724	3447.6	3346.2	426	426
Saving of primary fuel	0.7	107.7/286.7	15.3/41.7	30.5/81.22	29.6/78.8	3.8/10.03	3.8/10.03
energy, millions of GJ/year	0.4	14/338.5	2/48	3.96/95.9	3.8/93.1	0.5/11.85	0.5/11.85
Saving of natural gas,	0.7	3076.7	437	871.3	845.6	107.7	107.7
millions of m^3 of CH_4/year	0.4	400	57.1	113.14	108.6	14	14
Reduction in CO_2	0.7	1565.5/8169.4	222.4/1047.8	443.34/2314.32	430.3/2245.4	54.8/285.8	54.8/285.8
emission, millions of kg/year	0.4	203.6/9655.1	29.1/1368	57.58/2735.38	55.3/2655.5	7.1/338	7.1/338

Note. Numerator denotes indicator with respect to steam-gas plant with efficiency of 54%; denominator denotes indicator with respect to coal-fired plant with efficiency of 36%.

Figure 3 presents some results of an efficiency analysis of the two alternate schemes of gas-turbine-driven generating sets with extraction of process air after the compressor and a feed of exhaust gas into the combustion chamber of the turbine-driven set [4, 6]. Extraction of process air prior to the combustion chamber and its mixing with exhaust gas requires use of an additional turbo-machine (a blower on the cold side of the exhaust gas) to overcome the hydraulic resistance of the entire HNO_3 system.

The following parameters were used in analyzing the efficiency: an exhaust-gas temperature T_E = 1440°K prior to the combustion chamber; a temperature T_3 = 1023°K for the mixture of combustion products and exhaust gas prior to the turbine; a relative air extraction δ_A (the ratio of the extraction flow to the flow at the inlet to the system's compressor); polytropic efficiencies of η_{pv} = 90% for the compressor, and η_{pt} = 85% for the turbine; and a process-air flow m_A = 55 kg/sec. Curves of the effective capacity P_e of the system versus the thermal flux $\dot{Q}_{wyl}$ of exhaust gases are presented in Fig. 3 for a system with an output of 1000 tons of HNO_3/day.

It follows from Fig. 3 that the increased δ_A values make it possible to obtain elevated efficiencies with a simultaneous reduction in the electric power of the gas-turbine-driven generating set. For a compression ratio $\pi = 11$ and relative extraction $\delta_A = 0.7$, and interstage cooling of the compressor, η_{the} = 41%, and the power generated is 21 MW. When $\delta_A = 0.4$, the efficiency η_{the} = 33.5%, but the power of the turbine-driven generating set increases to 41 MW. The efficiency of the gas-turbine-driven set, which operates in accordance with a simple cycle, is 31.5% (when $\pi = 11$) and 32.5% (when $\pi = 15$).

The exhaust gases from the gas turbine are carried off with its own large amount of heat (see Fig. 3): $\dot{Q}_{wyl}$ = 36 MW when $\delta_A = 0.7$, and $\dot{Q}_{wyl}$ = 63 MW when $\delta_A = 0.4$. Complete utilization of this heat for process-steam generation alone, or for heating alone is inexpedient, not to mention that the charged waste-heat boiler, which is incorporated into a series of heat exchangers for the cooling of process gas (see Fig. 1), ensures high steam parameters for a heat output $\Delta\Phi_5$ = 20 MW owing to the temperature range of the gas (see Fig. 2). Of course, favorable conditions exist for a combined steam-gas cycle in the power system of the plant producing the nitric acid.

Figure 4 shows a schematic diagram combining the HNO_3-production system with gas and steam turbines, and subsequently with connected boilers. The potential power characteristics are presented in Table 2 (for simplification, it is assumed that the efficiency of the steam cycle is constant and equal to 32% for all solutions of the combined system). In the new scheme, the compressor-expander is replaced by a gas-turbine-driven generating set with process-air extraction and mixing of exhaust gas in the combustion chamber.

Table 3 illustrates the economic benefits accrued when the HNO_3-production system is integrated with the combined system of gas and steam turbines.

Table 3 does not indicate the annual reduction in NO_x emissions; they can be estimated, however, by comparing the total emission for operating plants, irrespective of the type of HNO_3-production system and convective type of combined steam-gas plant, with NO_x emissions in an HNO_3 system integrated with a steam-gas plant (having the same electric and heat capacity and the same productivity with respect to nitric acid). For a similar design of combustion chamber, a turbine-driven generating set with increased efficiency (integrated) provides for a reduction in NO_x emissions per unit of electric power, and one would expect similar emissions in an HNO_3-production system with similar technologies and method of NO_x reduction. The method used to mix the tail gas (in the combustion chamber of the turbo-system) may also affect the reduction in emission due to the fact that combustion of mixtures with a reduced oxygen content contributes to a reduction in the liberation of NO_x.

In conclusion, let us point out that success with implementation of the proposed means of lowering investment and energy outlays will depend to a large degree on the producer's readiness to incorporate into his HNO_3-production scheme gas turbines equipped to accommodate such structural changes as extraction of air from the compressor (frequently with intersectional cooling), and mixing of hot tail gas in a turbine or combustion chamber.

These changes are readily implemented in systems similar to aircraft designs (for example, a dual-stage compressor and turbine. The need for appropriate changes in gas turbines for industrial conditions is confirmed by what little published results of experimental investigations there are to date, which deal with the extraction of air from a circular chamber beyond the diffusor and prior to the multisectional combustion chamber [7, 8] and the mixing of low-calorie gases contaminated with air or nitrogen from the oxygen unit in the combustion chamber [9, 10].

Only the free power market of the independent energy producers (IPP) can help introduce appropriate changes in the design of gas turbines, especially for industrial use, and also carry out assessment of the savings realized in this case.

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